

DEHYDRATION OF BENZYL ALCOHOL ON GAMMA - ALUMINA

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By
B. C. SUTRADHAR

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DEPARTMENT OF CHEMICAL ENGINEERING
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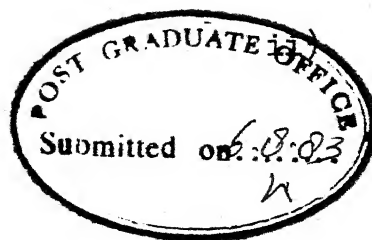
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CERTIFICATE

This is to certify that this work on "DEHYDRATION OF BENZYL ALCOHOL ON GAMMA ALUMINA" has been carried out under my supervision and that the same has not been submitted elsewhere for a degree.

August, 1983.


(D. Kunzru)
Professor
Department of Chemical Engg.,
Indian Institute of Technology,
Kanpur-208016

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-B.C.Sutradhar

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Abstract

The kinetics of the dehydration of benzyl alcohol have been studied over fresh γ - Al_2O_3 and pyridine loaded γ - Al_2O_3 . A small amounts of pyridine on the catalyst increased the conversions considerably contrary to expectations. The kinetic studies were made in the temperature range 563-623°K with both pure benzyl alcohol feed and benzyl alcohol containing water. The rate expressions

$$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_{RS} p_R)^2}$$

and

$$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_R p_R + K_S p_S)^2}$$

could adequately represent the experimental results for the cases $p_R = p_S$ (pure feed) and $p_R \neq p_S$ (mixed feed) respectively. The rate constants were affected significantly for the pyridine loaded γ - Al_2O_3 .

It seems that pyridine adsorbed selectively on the Lewis acid sites of Al_2O_3 and thereby promoted the reaction.

NOMENCLATURE

A	Reactant
C_A, C_W	Concentration of A and W
F_{A0}	Feed Rate of Reactant A, mol/hr
k	Rate Constant
k_A	kK_A
K	Equilibrium Constant
$K_A, K_R,$ K_S, K_W	Adsorption Equilibrium Constants of A, R, S and W
K_{RS}	$(K_R + K_S)$
$p_A, p_R,$ p_S, p_N	Partial Pressures of A, R, S and W, atm.
$-r_A$	Rate of Reaction of A, mol/g-hr
$-r_{A0}$	Rate of Reaction of A for $p_R = p_S = 0$
R, S	Reaction Products
W	Catalyst Weight, g.

CHAPTER 1

INTRODUCTION

Dehydration of alcohols particularly methanol, ethanol and propanol has been extensively studied in the last two decades. These dehydration reactions have generally been investigated on acidic catalysts such as alumina, silica, or silica-alumina. The catalytic dehydration of ethanol on alumina is a commercially proven process for the manufacture of ethylene. Although considerable work has been conducted on simple alcohols, very meagre data is available on the dehydration of higher alcohols on acidic catalysts.

For the design of any catalytic reactor not only are the kinetics and the selectivity of the main reaction important but the effect of various process variables on the catalyst deactivation due to poisoning and coking should also be considered.

Acidic catalysts are generally poisoned by organic bases and this has been conclusively demonstrated for the catalytic cracking of hydrocarbons. Catalyst poisoning on such type of reactions is very important in that a very small amount of base present in the feed poisons the acidic catalyst to a great extent, and the reaction rates are highly affected thereby. Moreover, depending upon the experimental conditions coke is also formed during catalytic dehydration of alcohols

and this deposits on the catalyst reducing the activity and changing the selectivity. Very little data is available on catalyst deactivation due to poisoning and coke deposition of dehydration reactions.

Catalyst poisoning experiments can also provide information on the nature of the active sites; the stronger sites being poisoned first. Catalytic poisoning can be modelled either in terms of separable or non-separable kinetics depending on the system.

The objective of this study was to investigate the kinetics of dehydration of benzyl alcohol on fresh γ -alumina and pyridine loaded γ -alumina. Benzyl alcohol was chosen as the reactant, because firstly, no data is available on this system and secondly, the product distribution is relatively simple so that the analysis is easier. Generally for aliphatic alcohols, alcohol is consumed due to two parallel reactions forming ether and olefin; in this case ether formation is the only reaction in which benzyl alcohol is consumed.

CHAPTER II

LITERATURE SURVEY

The dehydration of alcohols by acidic catalysts has been studied extensively as reviewed by Winfield (1) and Pines and Manassen (2). The catalysts used were SiO_2 , Al_2O_3 or $\text{SiO}_2/\text{Al}_2\text{O}_3$. Miller (3) investigated the dehydration of ethanol, n-propanol, and n-butanol and found that the rate of dehydration was controlled by a single site surface reaction. Bakshi and Gavallas (4) studied methanol and ethanol dehydration over fresh and poisoned $\text{SiO}_2/\text{Al}_2\text{O}_3$ and the data for both the cases could be represented by rate equation of the form

$$-r_A = \frac{k K_A C_A^{1/2}}{1 + K_A C_A^{1/2} + K_W C_W} \quad (1)$$

Knozinger et al (5) studied the kinetics of bimolecular ether formation from alcohols over alumina and proposed various models from a series of reaction mechanisms differing by one or more elementary steps.

Very little data are available on the dehydration of benzyl alcohol. Emert et al (6) dehydrated benzyl alcohols in dimethyl sulfoxide to prepare dibenzyl ether. Kinetic data for liquid or vapour phase dehydration has not been reported so far.

In the last few years attention has focussed on the study of the kinetics of catalyst deactivation and its importance in reactor design.

Figueras et al (7,8) investigated the kinetics of dehydration of methanol, ethanol and tertiary butyl alcohol over silica-alumina catalysts together with the effect of a variety of poisons on the catalyst and have presented a mechanistic interpretation of their results. Bakshi and Gavallas (4) reported that separable kinetics fails to describe some important effects of catalyst poisoning. Asua (9) found that the dehydration of isoamyl alcohol could be represented by a rate equation of the form

$$-r_A = \frac{k(p_A - p_R p_S / K)}{1 + K_A p_A + K_R p_R} \quad (2)$$

which corresponds to a mechanism controlled by the surface reaction on an active centre.

Corella and Asua (10) investigated the kinetics and mechanism of the deactivation by fouling of a silica-alumina catalyst in the gas phase dehydration of iso-amyl alcohol. The reported kinetic equation for the deactivation, is of the Langmuir-Hinshelwood type.

The poisoning of acidic catalysts by organic bases or by coke deposition has been investigated by various workers (11,12,13,14).

The general conclusion from these results was that two different types of active sites on alumina were responsible for the olefin isomerization and the alcohol dehydration. It was argued that the dehydration reaction occurs on only weakly acidic or even non-acidic sites.

Knozinger and Stolz (12) studied the dehydration of t-butanol and reported that pyridine is solely held by Lewis acid sites under their experimental conditions and hence the rate of isobutylene formation from t-butanol was essentially independent of the degree of poisoning.

From the survey we see that no data are available for benzyl alcohol dehydration either on fresh catalyst or on the poisoning kinetics.

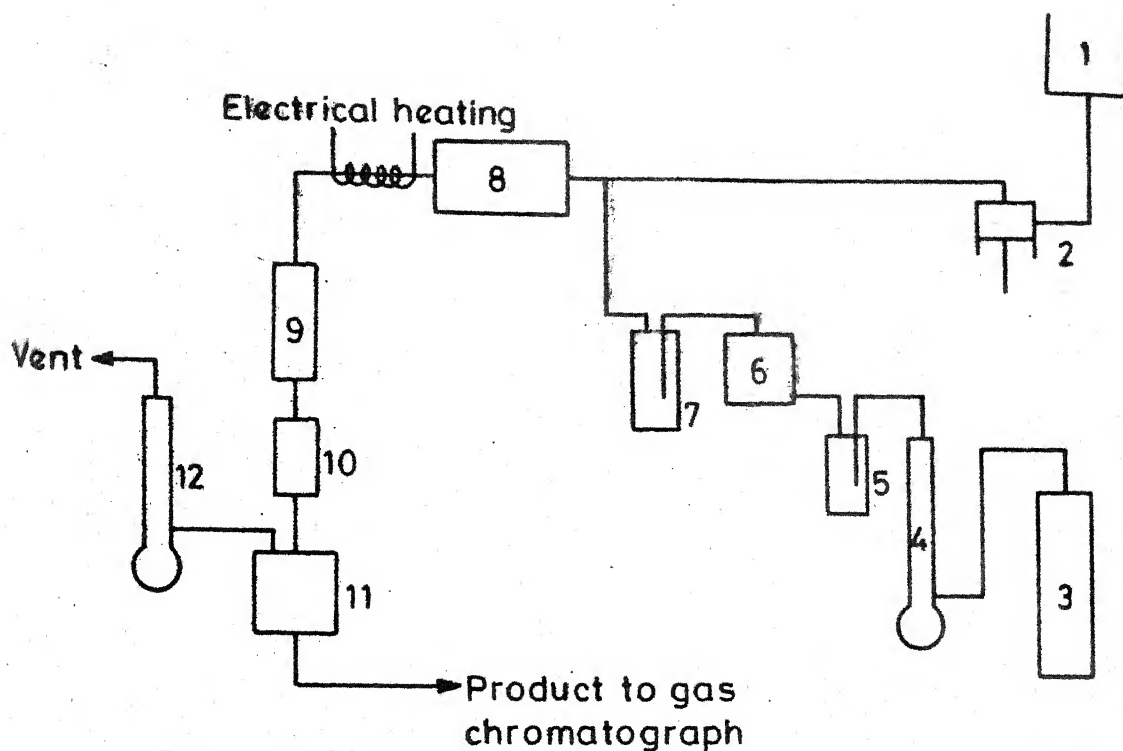
CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

3.1 Experimental Apparatus:

The catalytic vapour phase dehydration of benzyl alcohol was conducted in a vertical fixed bed reactor and a schematic diagram of the experimental setup is shown in Figure 1. The reactor was made from a 16 mm i.d., 50 cms. long stainless steel tube. The catalyst was positioned at 27 cms. from the top of the reactor with the help of a 30 B.S.S. stainless steel wire mesh. The temperature in the catalyst bed was measured using a chromel alumel thermocouple placed in a co-axial 3.2 mm i.d., 34 cms. long stainless steel thermowell. The millivolt signal from the thermocouple was measured using a HIL 2301 digital panel meter which was accurate to within ± 0.01 mV. The reactor was placed inside an electrically heated furnace, which was constructed by winding Kanthal wire over a ceramic tube and insulated with magnesia powder. The capacity of furnace was 2.8 KW. The temperature of the reactor was controlled with the help of a temperature controller (LAXSONS).

Liquid benzyl alcohol was fed with the help of a calibrated metering pump (LAPP) having a range of 0.3 to 20 ml/min. The liquid reactant before entering the reactor was vapourized and preheated in a preheater. The preheater was placed horizontally in another electrically heated furnace with a capacity of 2 KW.



- | | |
|---------------------------|---------------------|
| 1. Benzyl alcohol storage | 7. Empty guard tube |
| 2. Metering pump | 8. Preheater |
| 3. Nitrogen cylinder | 9. Reactor |
| 4,12. Soap bubble meter | 10. Condenser |
| 5. Deoxygenator | 11. Receiver |
| 6. Silica gel drier | |

Fig. 1 - Schematic diagram of the experimental setup.

In order to prevent condensation of the benzyl alcohol vapour in the connecting line between the preheater and the reactor, this line was also electrically heated with a coil of Kanthel wire of capacity 1 KW and was well insulated.

Provision was made for diluting the feed with inert nitrogen before the inlet of the preheater. The nitrogen from the cylinder was deoxygenated using alkaline pyrogallol solution and subsequently dried by passing through a bed of silica-gel. The flow rate of the nitrogen was measured using a soap-bubble meter in the flow path. To prevent the back flow of liquid reactant into the nitrogen line an empty guard tube was placed between the reactor and silica-gel dryer. The effluent from the reactor was cooled by a condenser using ice-cold water and the liquid condensate was analysed on a gas chromatograph.

3.2 Analysis:

The unreacted benzyl alcohol and any benzaldehyde and toluene formed in the reaction were analysed on a CIO gas chromatograph using a thermal conductivity detector. The analysis was performed on a 6.25 mm i.d., 300 cms. long copper tube packed with 5% SE 30 on Chromosorb W (60/80 mesh). The carrier gas was nitrogen and the oven and the injector temperatures were 120 and 180°C, respectively. The nitrogen flow-rate through the column was 50 ml/min.

3.3 Experimental Procedure:

The dehydration reaction on fresh γ - Al_2O_3 was studied in the temperature range 563-623°K. The partial pressures of benzyl alcohol, nitrogen and water were varied over the range 0.65 - 0.85, 0 - 0.35 and 0 - 0.15 atms., respectively. The total pressure in the reactor was maintained at 1 atm. The catalyst used was prepared by crushing and sieving 3.2 mm. γ - Al_2O_3 pellets (Harshaw Al 0104T Alumina catalyst; surface area - 100 m^2/g , pore volume - 0.39 cm^3/g and Al_2O_3 content - 99%). The size fraction employed was 10/16 B.S.S. (average particle size : 1.34 mm).

An experimental run was initiated by placing a weighed amount of catalyst in the reactor. Depending upon the conditions desired the catalyst was used as such or diluted with inert ceramic beads of the same size. The heating of the reactor, preheater and the connecting line was started. The heating rate was kept low initially and increased gradually till the desired steady state was attained. The reactor was maintained at this temperature for 5-6 hrs. in order to obtain a uniform temperature in the catalyst bed. After that the setup was thoroughly flushed with nitrogen and the nitrogen flow rate fixed at the desired value. After 15-20 minutes, benzyl alcohol feeding was started.

The liquid products and the unreacted benzyl alcohol started collecting in the graduated receiver after 15-20 minutes.

It was observed that the conversion of benzyl alcohol attained a steady state value only after approximately 1 hour from the start of benzyl alcohol feeding. The steady state mass balance data was therefore taken after the steady state had been achieved. The flow rate of the gaseous effluent from the outlet of the condenser was checked and no discernable change from the inlet nitrogen flow rate could be detected, i.e., the amount of gaseous products was negligible.

After each run the setup was again flushed thoroughly with nitrogen in order to remove any residual liquid in the reactor. The setup was then cooled and the reactor was detached. The catalyst bed was taken out from the reactor and stored.

The same catalyst bed was not used for more than three hours because of catalyst deactivation due to coke deposition and this has^{been} discussed in detail in the Results and Discussion Chapter.

3.4 Preparation of Pyridine Loaded Catalyst:

To study the effect of pyridine loading on alumina, the fresh alumina catalyst was treated as follows:

A 2% (v/v) solution of pyridine in absolute alcohol (95%) was prepared and in 100 ml of this solution about 10 g of the catalyst particles were kept immersed for $2\frac{1}{2}$ hours. The catalyst was then filtered, dried in air and then kept overnight

in an air oven at 125°C. The filtrate was diluted further with the 95% alcohol and the concentration and hence the amount of pyridine was determined from a UV absorption measurement of the solution. The difference in the amounts of pyridine between the original solution and the filtrate was the amount adsorbed on the alumina. Further loss in pyridine due to heating in the reactor was estimated from the TGA (Thermogravimetric analysis) derivatogram of the sample and that of fresh alumina.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Reaction Chemistry:

The possibility of this dehydration reaction was the outcome of some studies on the dehydrogenation reaction of benzyl alcohol on nickel oxide/alumina and nickel/kieselghur. In such cases the dehydrogenation reaction was far less than expected and in all cases a higher boiling compound was found in large proportions. The compound was separated from the reaction product by fractionation under reduced pressure. The boiling point measured was 110°C at 0.8 mmHg which corresponds to 298°C at 760 mmHg. Interestingly, the composition of the reaction mixture was observed to change on standing, particularly on exposure to air. The decomposition products were benzaldehyde and toluene. An NMR report (Figure 2) was obtained for the sample and peaks were obtained at 4.47 δ (s) and 7.25 δ (s) which corresponds to that of dibenzyl ether (the peaks for the standard being at 4.49 δ (s) and 7.24 δ (s)). Moreover, the boiling point of dibenzyl ether is 298°C.

Some runs were then taken with pure $\star \text{Al}_2\text{O}_3$ as catalyst and the same fraction was isolated by distillation (checked by TLC). At low temperatures dibenzyl ether was the only product although at higher temperatures small amounts of benzaldehyde and toluene together with minute amounts of higher boiling compounds

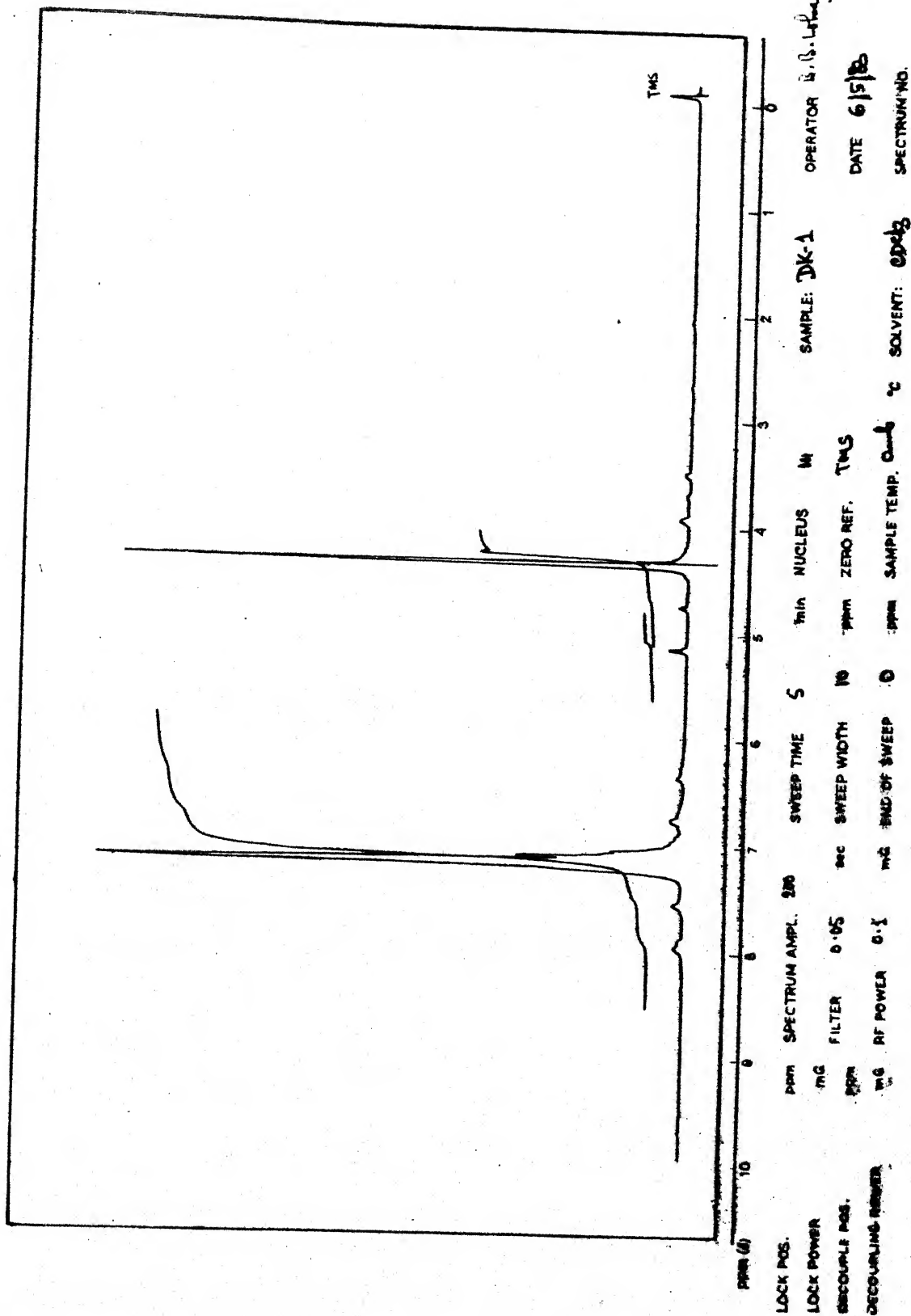
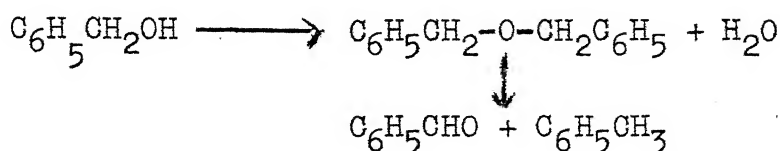


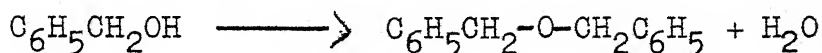
Fig. 2 - NMR Report.

were also formed (observed during distillation and on TLC). It was observed that the higher the temperature and concentration of the ether higher was the amount of benzaldehyde and toluene formed.

Thus the overall reaction for benzyl alcohol dehydration can be represented as



Moreover, for the conditions used in this study, the amounts of benzaldehyde and toluene were always less than 2 mole % and thus the above reaction could be simplified as



4.2 Preliminary Experiments:

(1) Catalyst Deactivation by Coke Formation:

Coke formation is a very common phenomena in catalytic organic reactions, particularly at high temperatures. The coke formed deposits on the catalyst thereby reducing the catalyst activity. Moreover, for a flow reactor, some time is required for the steady state to be attained. In order to determine the proper duration of the experimental runs, the effect of the run time on benzyl alcohol conversion was investigated and a typical result is shown in Figure 3. As shown in this figure, the conversion gradually increased with

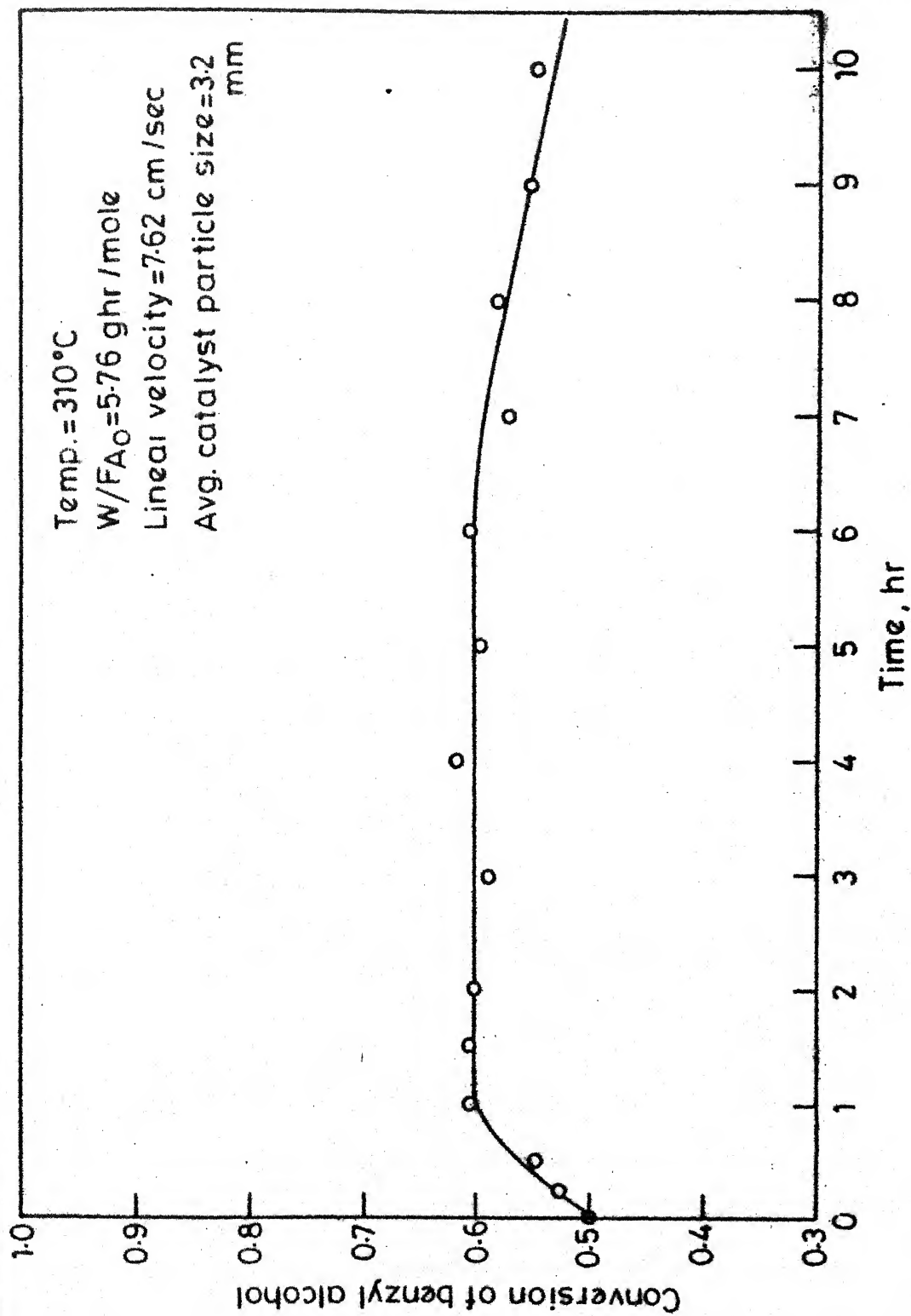


Fig. 3 - Conversion of benzyl alcohol vs. run time.

time and attained the steady state value after approximately 1 hour. Thereafter, the conversion was virtually constant till a run time of 6 hours after which it gradually decreased due to coke deposition on the catalyst. Thus, for the main kinetic runs, the steady state conversion data was measured after one hour had elapsed from the start of the run. Moreover, the bed of catalyst was not used for more than a total of 3 hours run time.

(2) External and Internal Mass Transfer Limitations:

To ensure the absence of mass transfer limitations, preliminary runs were conducted to determine the conditions for which these resistances were negligible. Since mass transfer resistances are more likely to affect the reaction at high temperatures, these preliminary runs were performed at a temperature higher or equal to the maximum temperature used for the main runs.

To study the effect of external mass transfer resistances on the conversion, experiments were performed for different linear gas velocities through the bed keeping space time (W/F_{A0}), temperature and partial pressure of benzyl alcohol constant and the results are shown in Figure 4. Conversion increased with increasing linear velocity till 6.5 cm/s beyond which the linear velocity did not affect the conversion of benzyl alcohol. Therefore for all subsequent runs, the linear velocity was kept more than 6.5 cm/s ensuring

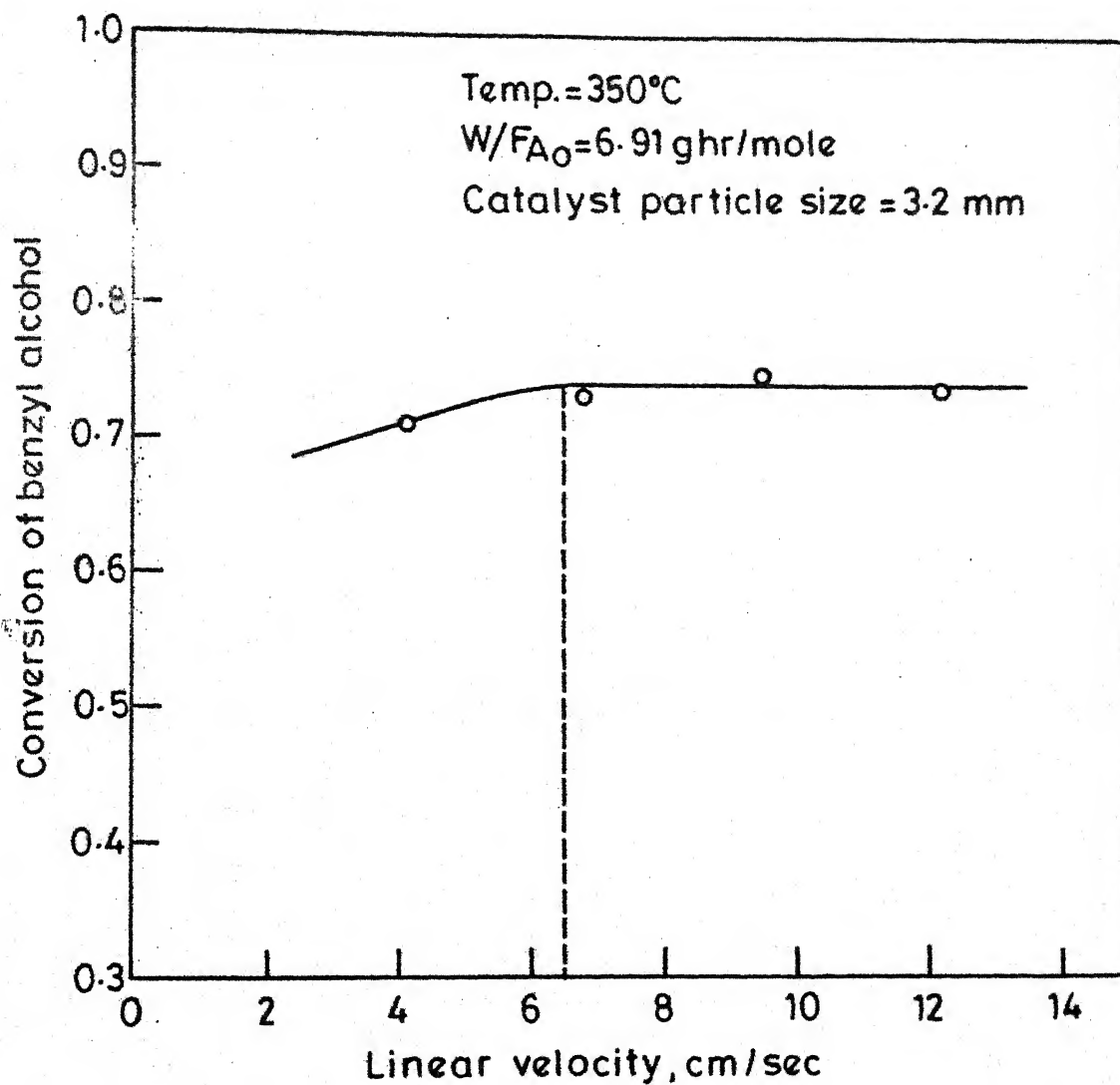


Fig. 4 - Effect of linear velocity on conversion of benzyl alcohol.

that external mass transfer resistance did not affect the conversion.

The importance of internal diffusion was checked by conducting runs at constant W/F_{A0} , linear velocity, temperature and partial pressure of benzyl alcohol for different catalyst particle sizes. The effect of catalyst size on conversion at fixed condition is shown in Figure 5. Conversion increased initially with a decrease in particle size but identical conversions were obtained for particle size smaller than or equal to 1.5 mm. Thus, for subsequent runs, the average catalyst particle size was chosen to be 1.34 mm (10/16 B.S.S.).

4.3 Kinetics Over Fresh Catalyst:

Kinetic runs over fresh alumina catalyst were taken for various temperatures, inlet partial pressures of benzyl alcohol and space times (W/F_{A0}), covering the ranges 563-623°K, 0.65-0.85 atms, 0.15 - 6.91g hr/mole respectively.

The inlet partial pressure of benzyl alcohol was varied by changing the percentage of inert nitrogen in the feed. The partial pressure of benzyl alcohol could not be reduced below 0.65 atm. due to the limitations in the heating capacities of the preheater and the reactor.

Different space time (W/F_{A0}) could be fixed either by varying the weight of catalyst (W) in the catalyst bed or by

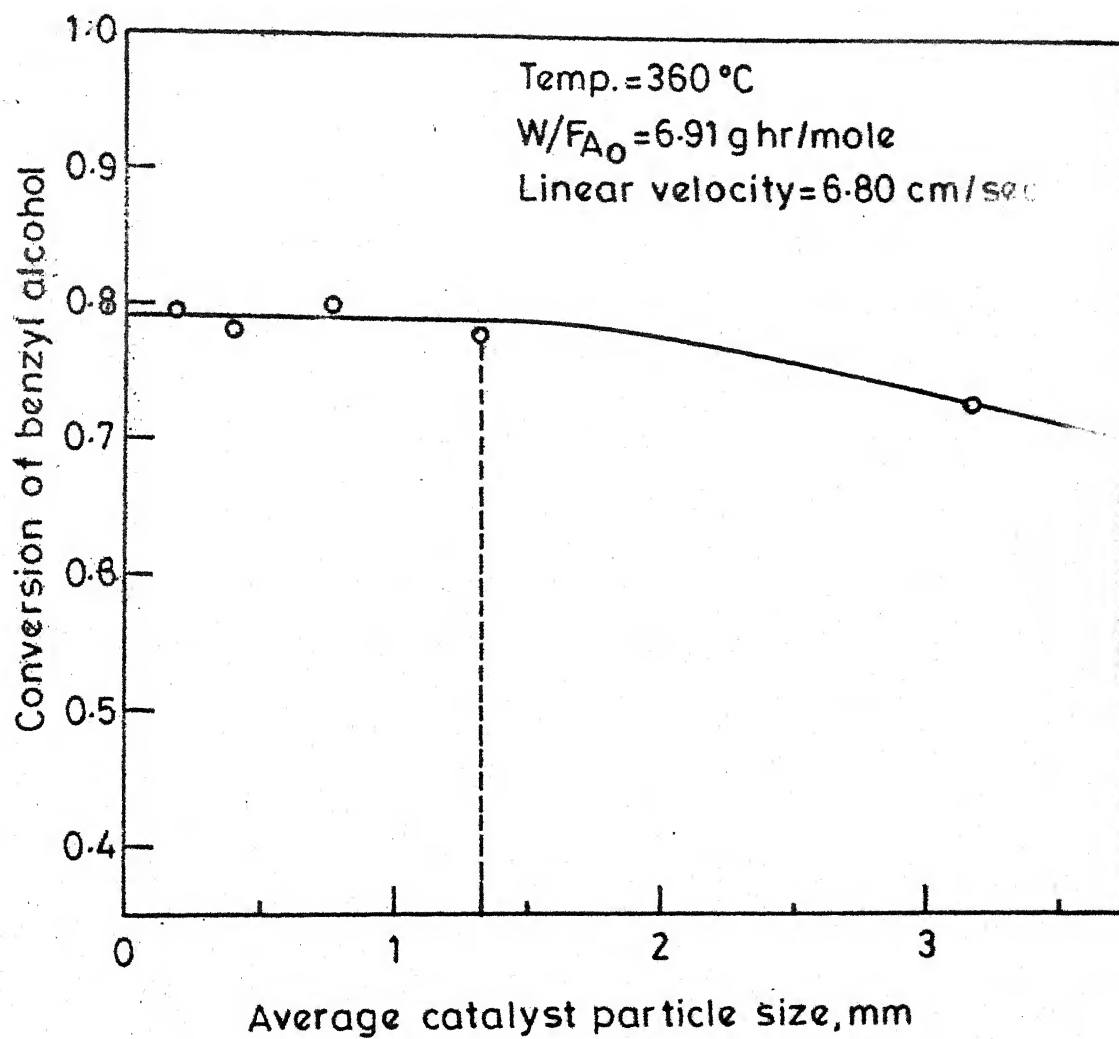


Fig. 5 - Variation of benzyl alcohol conversion with average catalyst particle size.

changing the feed flow rate (F_{A0}). However, higher flow rates of benzyl alcohol gave erroneous results; the conversions either did not change or sometimes even decreased with increase in space time. This was again due to heating limitations of the setup so that the liquid feed was not properly heated at the higher flow rates. Thus, the space time was varied by changing the weight of the active catalyst. The total weight of the bed was kept constant at 5g by diluting with inert ceramic beads. The active catalyst content of the bed varied from 2% to 100%. At low flow rates the conversion measured by either varying W or F_{A0} was the same.

The variation of conversion with space time at different temperatures for a feed benzyl alcohol partial pressure of 0.85 atm is shown in Figure 6. The conversion increases with increase in both space time and temperature; with space time, the rate of change of conversion is initially high and decreases at higher values.

Below 583°K, the only products detected were dibenzyl ether and water. However, above 583°K some benzaldehyde and toluene were also detected. The maximum amount of these secondary products did not exceed 2 mole% of the products. The water produced in the reaction could not be measured accurately because the water droplets remained dispersed in the condensed reactor effluent.

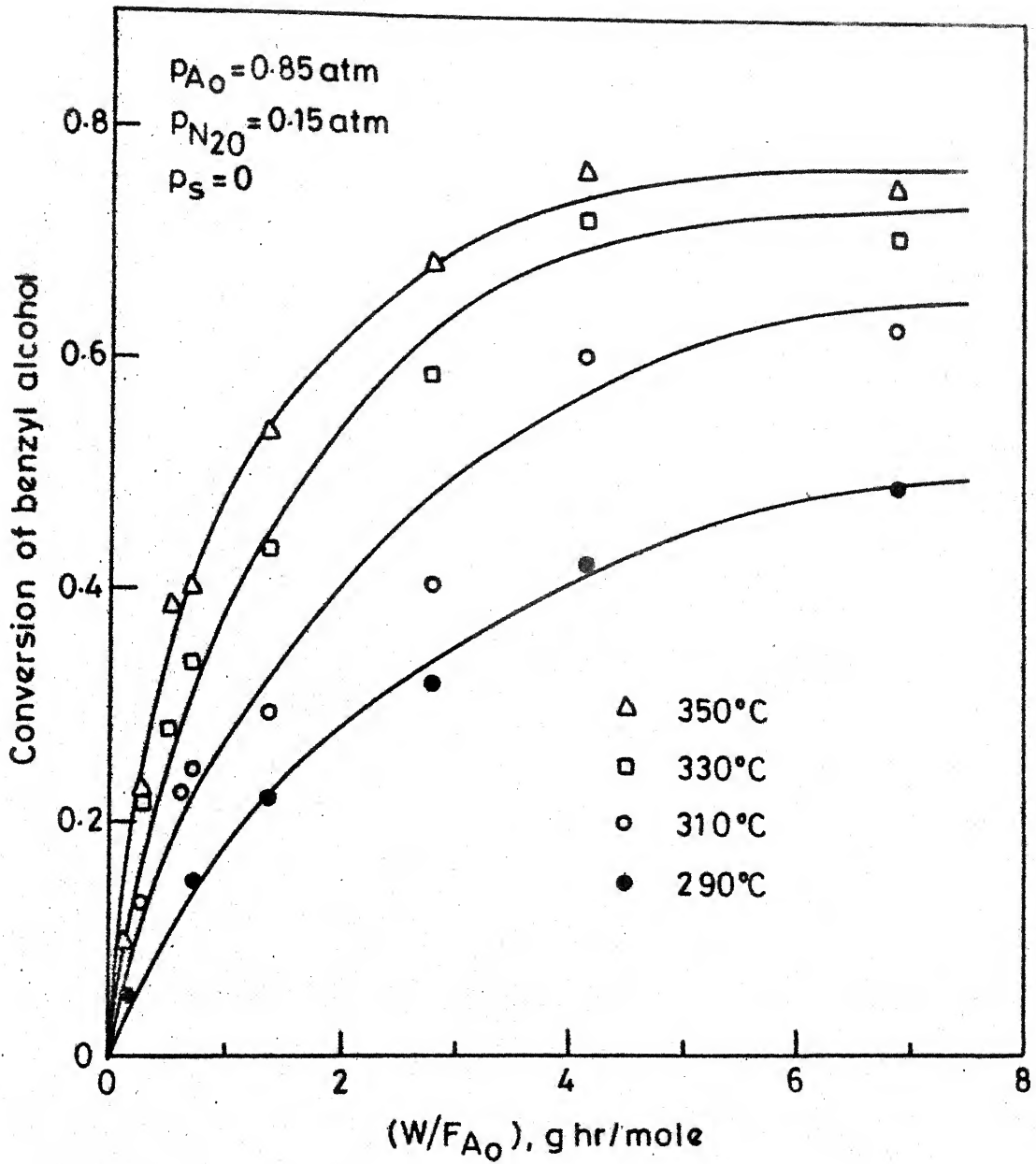


Fig. 6 - Effect of temperature on conversion of benzyl alcohol for pure benzyl alcohol feed.

Figure 7 shows the effect of inlet benzyl alcohol partial pressure on the conversion. The total pressure was maintained at 1 atm. As expected, for the same space time, conversion increased with increasing inlet partial pressure of benzyl alcohol.

Since water was one of the products of the reaction it is likely to have some effect on the reaction. To study the effect of water on the kinetics, some runs were conducted in which small amounts of water were mixed with the liquid benzyl alcohol feed. Large variation in the partial pressure of water in the feed could not be studied mainly because of the limitations in the experimental setup and also because of the very low solubility (3.46% v/v) of water in benzyl alcohol.

The experiments were performed at 563, 583, 603 and 623°K with the inlet mole fraction of water fixed at 0.15 and the results are shown in Figure 8. A comparison of Figure 6 and 8 shows that at all temperatures and space times, water in the feed significantly reduces the conversion. Similar runs could not be performed with the other reaction product (dibenzyl ether) because this product decomposes to benzaldehyde and toluene on exposure to air.

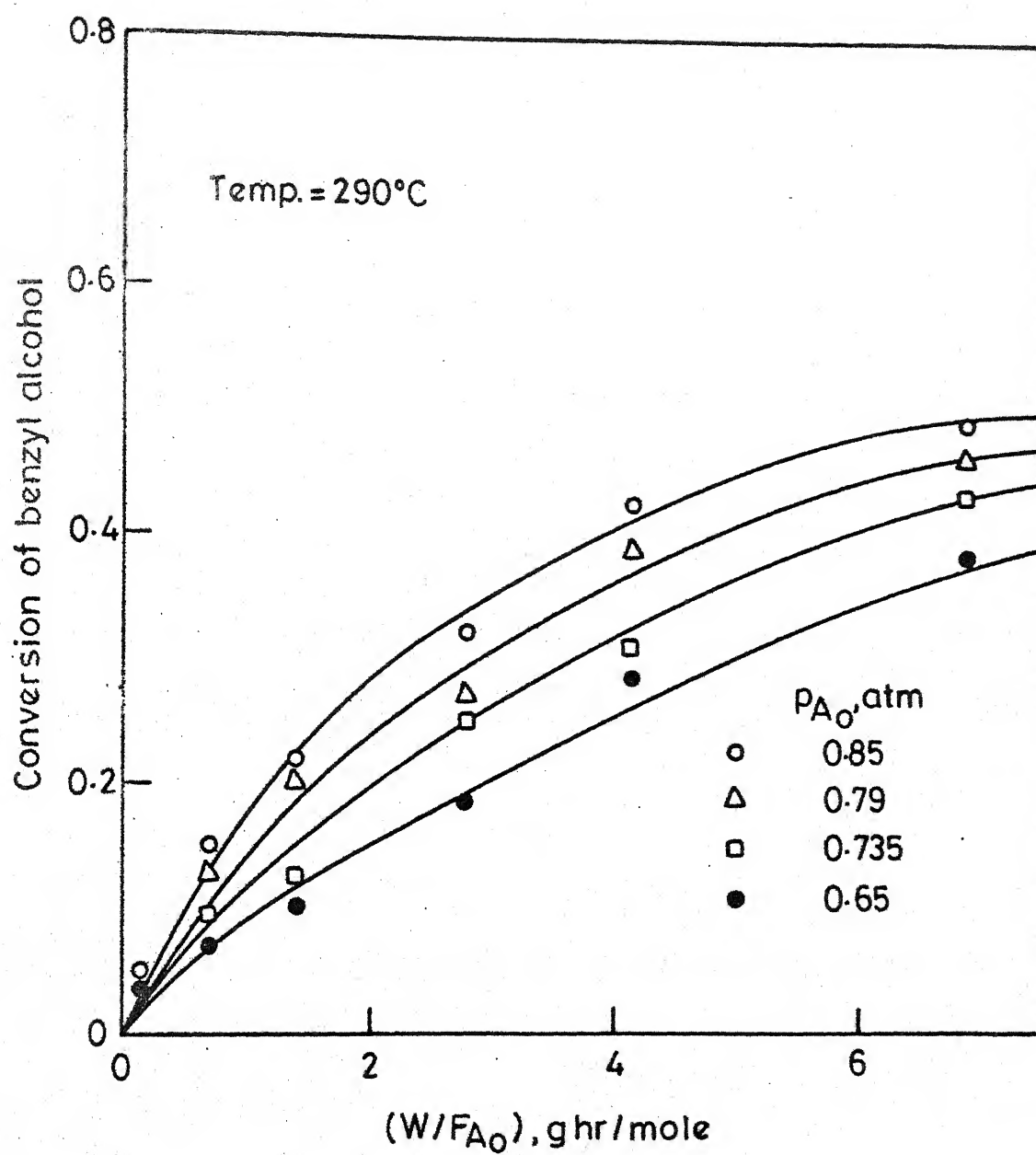


Fig. 7 -Effect of inlet partial pressure of benzyl alcohol on the conversion of benzyl alcohol.

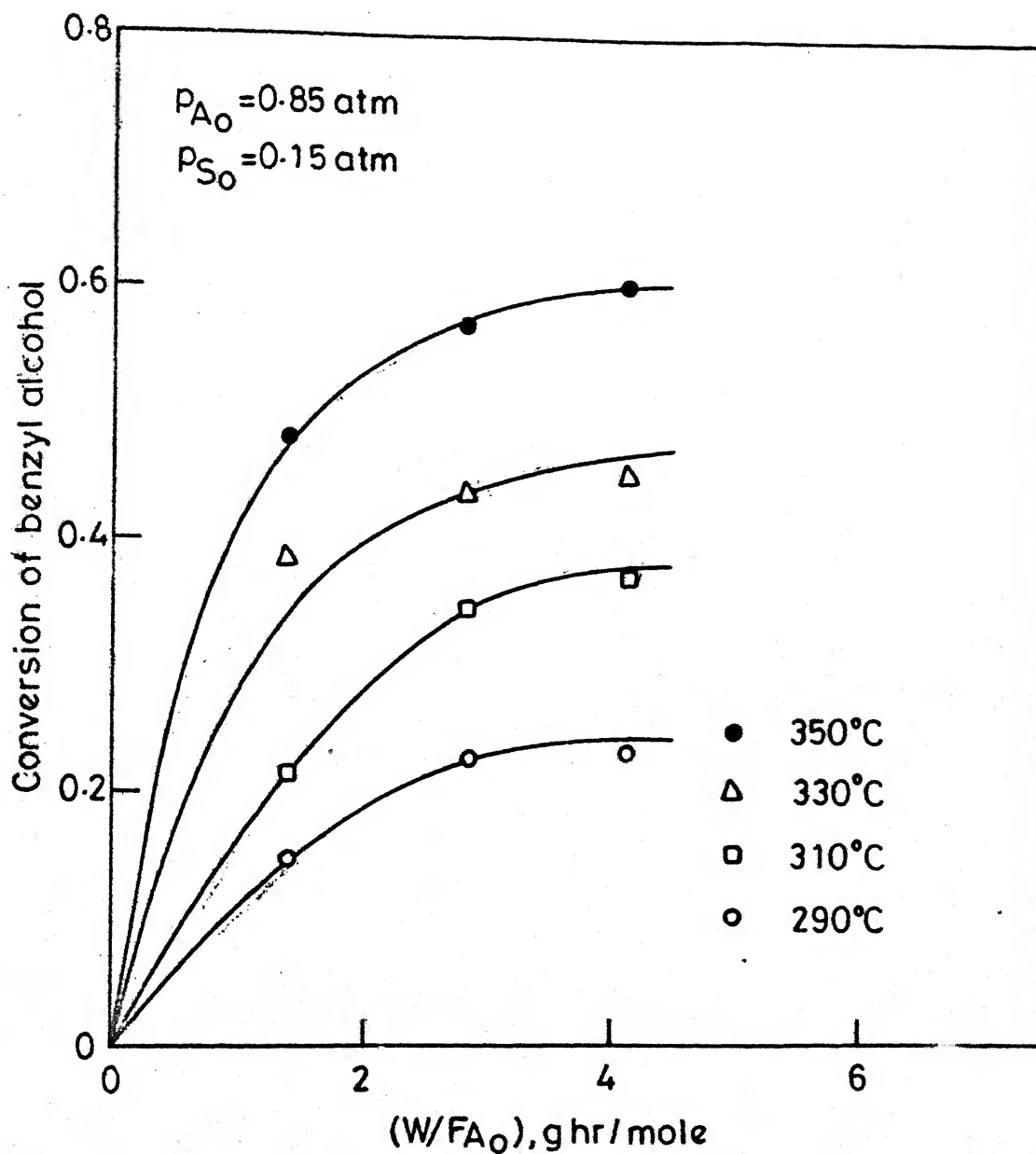


Fig. 8 - Effect of water in the benzyl alcohol on the conversion of benzyl alcohol at different temperatures.

4.4 Kinetics Over Pyridine Loaded Catalyst:

In order to study the effect of pyridine loading on γ -alumina, catalyst sample was prepared using the procedure given earlier. The pyridine loading on the catalyst was determined by measuring the volume and pyridine concentration of the filtrate. For this a UV absorption measurement was done for the filtrate. From the known initial concentration of pyridine, the pyridine loading on the catalyst was found to be 0.022 g/g of catalyst which when corrected for loss due to heating in the reactor came to 0.02 g/g alumina.

Experimental runs were taken at various temperatures with either pure benzyl alcohol or a mixture of water and benzyl alcohol as the feed. The variation of conversion with space time for the temperature levels investigated are plotted in Figures 9 and 10. Unexpectedly, it was found that the conversions with pyridine loaded catalysts for all the conditions were appreciably higher than those with fresh catalyst as can be seen by comparing Figures 6 and 9. For instance, at a temperature 563°K, inlet partial pressure of benzyl alcohol of 0.735 atm. and space time 2.76g hr/mole the conversion for fresh catalyst was 27% whereas for the pyridine loaded catalyst the conversion was 45.5%.

Similar enhancement in reaction rate for pyridine loaded Al_2O_3 has been reported for isobutanol dehydration (15) where the phenomenon was ascribed to the fact that pyridine

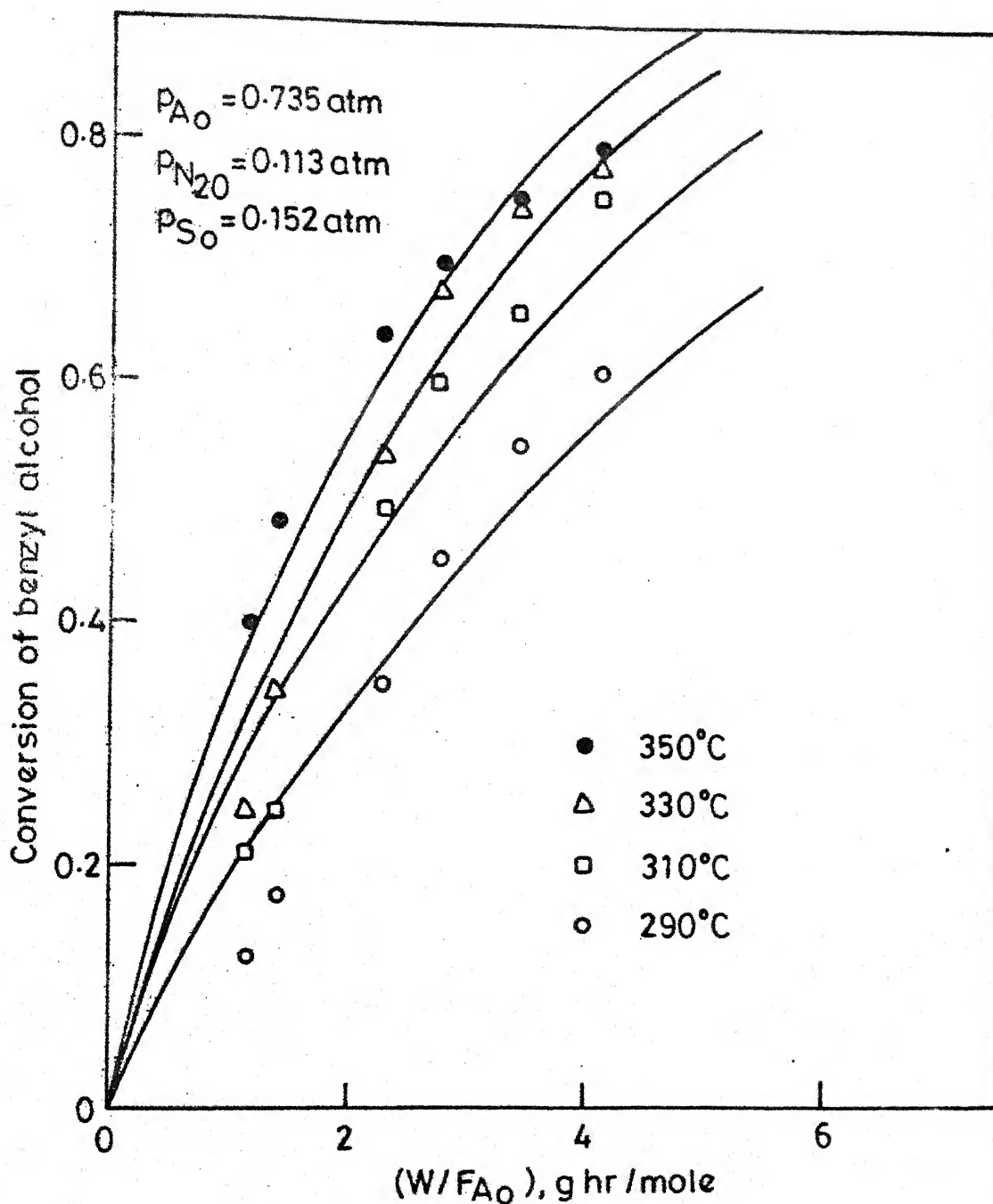


Fig. 9 - Effect of temperature on the conversion of benzyl alcohol for catalyst loaded with pyridine.

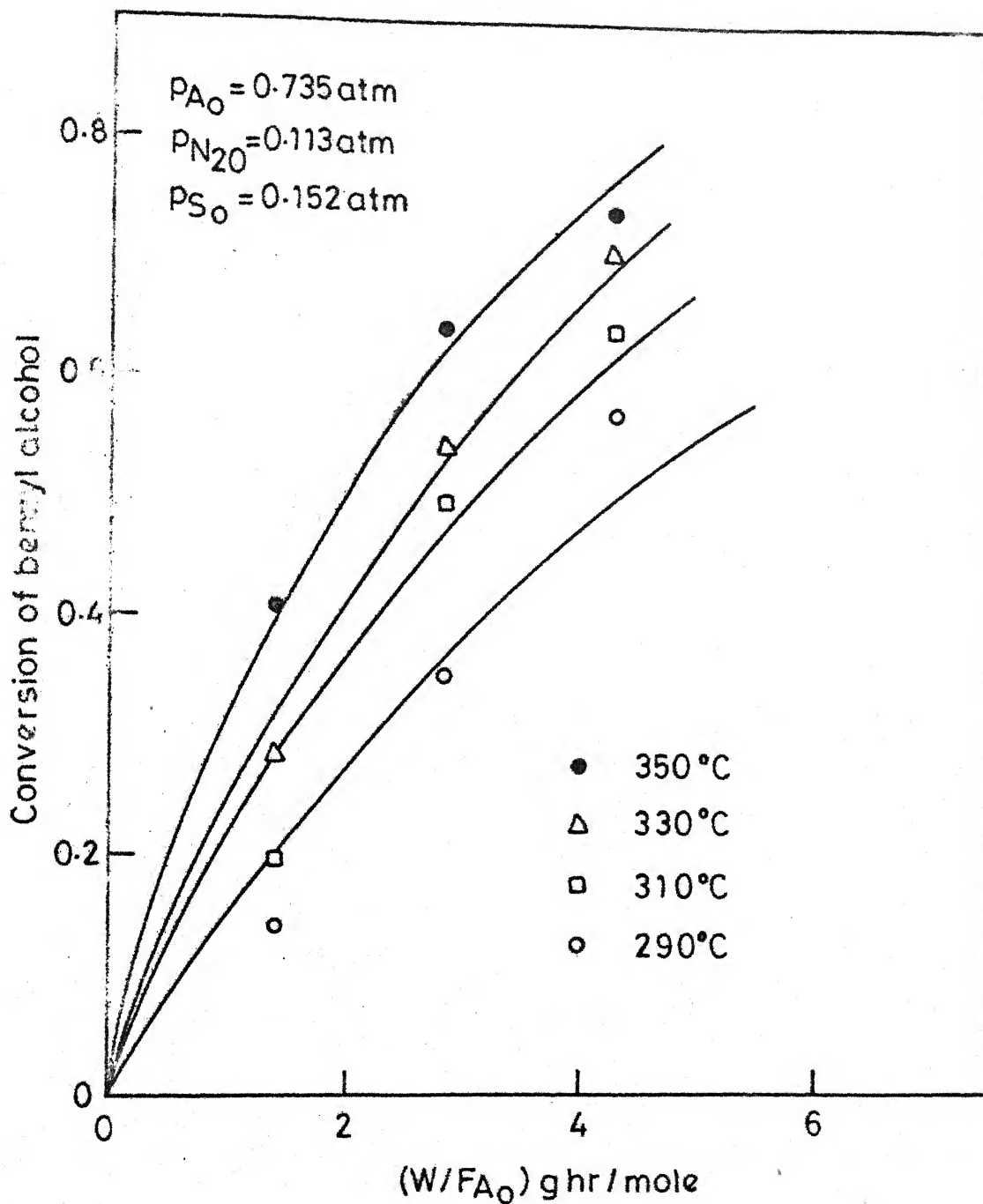


Fig. 10 - Effect of water in the feed benzyl alcohol on the conversion of benzyl alcohol for catalyst loaded with pyridine.

occupied the Lewis acid sites of the alumina catalyst which were of no importance for alcohol dehydration. Rather the preadsorbed pyridine leads to the increased surface concentration of the molecular form of adsorbed alcohol and thus increases the rate of reaction.

CHAPTER V

MODEL DISCRIMINATION AND PARAMETER ESTIMATION

As discussed earlier, the benzyl alcohol conversions varied from 3.5 to 76.5% and therefore the reactor was operating in the integral mode. Writing a mass balance for the reactant, denoted by A, in a differential element of the catalyst bed, we obtain

$$F_{A0} dX_A = -r_A dW \quad (1)$$

or

$$-r_A = \frac{dX_A}{d(W/F_{A0})} \quad (2)$$

The differential method of analysis was used and the rate of reaction was calculated by measuring the slope of the conversion vs. space time plots at various points. The variation of the rate of reaction with partial pressure of the reacting components for pure benzyl alcohol feed and feed containing water is shown in Tables 1 and 2, respectively. Attempt was then made to fit these rate data to models derived on the basis of various Langmuir-Hinshelwood mechanisms.

The dehydration of benzyl alcohol may be represented as

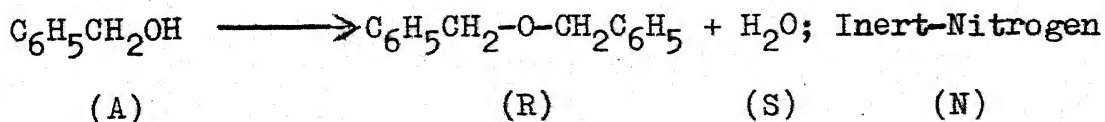


TABLE 1

Rate and Partial Pressure Data for Pure Benzyl Alcohol
Feed For Fresh Catalyst

Temperature = 623°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	1.046	0.848	0.000	0.000	0.152
0.25	0.21	0.657	0.670	0.089	0.089	0.152
0.50	0.34	0.416	0.558	0.144	0.144	0.152
0.75	0.42	0.272	0.487	0.180	0.180	0.152
1.00	0.48	0.191	0.439	0.240	0.240	0.152
1.50	0.56	0.124	0.375	0.236	0.236	0.152
2.00	0.61	0.101	0.328	0.260	0.260	0.152
2.50	0.66	0.082	0.289	0.279	0.279	0.152
3.00	0.69	0.061	0.258	0.295	0.295	0.152
3.50	0.72	0.044	0.236	0.306	0.306	0.152
4.00	0.74	0.031	0.221	0.314	0.314	0.152
4.50	0.75	0.021	0.021	0.319	0.319	0.152
5.00	0.76	0.013	0.202	0.323	0.323	0.152
5.50	0.77	0.006	0.198	0.325	0.325	0.152
6.00	0.77	0.003	0.196	0.326	0.326	0.152

Contd....

Table 1 (Continued):

Temperature = 603°K.

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.700	0.848	0.000	0.000	0.152
0.25	0.14	0.476	0.725	0.061	0.061	0.152
0.50	0.24	0.342	0.640	0.104	0.104	0.152
0.75	0.32	0.262	0.577	0.136	0.136	0.152
1.00	0.38	0.214	0.526	0.161	0.161	0.152
1.50	0.47	0.162	0.448	0.200	0.200	0.152
2.00	0.54	0.127	0.387	0.230	0.230	0.152
2.50	0.60	0.096	0.340	0.254	0.254	0.152
3.00	0.64	0.070	0.305	0.272	0.272	0.152
3.50	0.67	0.052	0.279	0.284	0.284	0.152
4.00	0.69	0.039	0.260	0.294	0.294	0.152
4.50	0.71	0.027	0.246	0.301	0.301	0.152
5.00	0.72	0.015	0.237	0.305	0.305	0.152
5.50	0.72	0.007	0.233	0.308	0.308	0.152
6.00	0.73	0.009	0.230	0.309	0.309	0.152

Contd.....

Table 1 (Continued):

Temperature = 583°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.550	0.848	0.000	0.000	0.152
0.25	0.11	0.335	0.755	0.046	0.046	0.152
0.50	0.18	0.226	0.697	0.075	0.075	0.152
0.75	0.23	0.177	0.655	0.096	0.096	0.152
1.00	0.27	0.157	0.620	0.114	0.114	0.152
1.50	0.34	0.141	0.557	0.145	0.145	0.152
2.00	0.41	0.119	0.501	0.173	0.173	0.152
2.50	0.46	0.091	0.456	0.196	0.196	0.152
3.00	0.50	0.070	0.423	0.213	0.213	0.152
3.50	0.53	0.061	0.395	0.226	0.226	0.152
4.00	0.56	0.057	0.370	0.239	0.239	0.152
4.50	0.59	0.049	0.348	0.250	0.250	0.152
5.00	0.61	0.036	0.329	0.259	0.259	0.152
5.50	0.63	0.025	0.317	0.265	0.265	0.152
6.00	0.64	0.029	0.306	0.271	0.271	0.152

Contd....

Table 1 (Continued):

Temperature = 563°K

W/F_{Ao}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.213	0.848	0.000	0.000	0.152
0.25	0.05	0.199	0.804	0.022	0.022	0.152
0.50	0.10	0.179	0.764	0.042	0.042	0.152
0.75	0.14	0.159	0.728	0.060	0.060	0.152
1.00	0.18	0.138	0.697	0.075	0.075	0.152
1.50	0.24	0.103	0.646	0.101	0.101	0.152
2.00	0.28	0.080	0.648	0.120	0.120	0.152
2.50	0.32	0.067	0.577	0.135	0.135	0.152
3.00	0.35	0.060	0.550	0.149	0.149	0.152
3.50	0.33	0.056	0.526	0.161	0.161	0.152
4.00	0.41	0.050	0.503	0.172	0.172	0.152
4.50	0.43	0.043	0.483	0.182	0.182	0.152
5.00	0.45	0.036	0.467	0.190	0.190	0.152
5.50	0.46	0.020	0.453	0.197	0.197	0.152
6.00	0.48	0.025	0.441	0.203	0.203	0.152

Contd....

TABLE 2Rate and Partial Pressure Data for Feed Benzyl Alcohol
Containing Water

Temperature = 623°K

W/F_{Ao}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.656	0.848	0.000	0.152	0.000
0.25	0.15	0.526	0.722	0.063	0.215	0.000
0.50	0.26	0.404	0.624	0.112	0.264	0.000
0.75	0.35	0.298	0.549	0.149	0.301	0.000
1.00	0.41	0.212	0.496	0.176	0.328	0.000
1.50	0.49	0.104	0.432	0.208	0.360	0.000
2.00	0.53	0.062	0.398	0.225	0.377	0.000
2.50	0.56	0.051	0.374	0.237	0.389	0.000
3.00	0.58	0.038	0.355	0.246	0.398	0.000
3.50	0.59	0.014	0.344	0.252	0.404	0.000
4.00	0.60	0.020	0.339	0.254	0.406	0.000

Contd....

Table 2 (Continued):

Temperature = 603°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.432	0.848	0.000	0.152	0.000
0.25	0.10	0.344	0.766	0.041	0.193	0.000
0.50	0.17	0.274	0.701	0.073	0.225	0.000
0.75	0.23	0.217	0.649	0.099	0.251	0.000
1.00	0.28	0.176	0.608	0.120	0.272	0.000
1.50	0.35	0.110	0.549	0.149	0.301	0.000
2.00	0.39	0.071	0.512	0.168	0.320	0.000
2.50	0.42	0.046	0.487	0.180	0.333	0.000
3.00	0.44	0.029	0.472	0.188	0.340	0.000
3.50	0.45	0.019	0.461	0.193	0.345	0.000
4.00	0.46	0.019	0.453	0.197	0.349	0.000

Contd....

Table 2 (Continued):

Temperature = 583°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.239	0.848	0.000	0.152	0.000
0.25	0.05	0.164	0.806	0.021	0.173	0.000
0.50	0.09	0.146	0.774	0.037	0.189	0.000
0.75	0.12	0.145	0.743	0.052	0.204	0.000
1.00	0.16	0.143	0.712	0.068	0.220	0.000
1.50	0.23	0.119	0.656	0.096	0.248	0.000
2.00	0.28	0.092	0.612	0.118	0.270	0.000
2.50	0.32	0.077	0.576	0.136	0.288	0.000
3.00	0.35	0.053	0.547	0.150	0.302	0.000
3.50	0.37	0.008	0.534	0.157	0.309	0.000
4.00	0.38	0.076	0.526	0.161	0.313	0.000

Contd....

Table 2 (Continued):

Temperature = 563°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.163	0.848	0.000	0.152	0.000
0.25	0.03	0.112	0.820	0.014	0.166	0.000
0.50	0.06	0.102	0.797	0.025	0.177	0.000
0.75	0.08	0.101	0.776	0.036	0.188	0.000
1.00	0.11	0.098	0.754	0.046	0.198	0.000
1.50	0.15	0.075	0.717	0.065	0.217	0.000
2.00	0.18	0.052	0.690	0.079	0.231	0.000
2.50	0.21	0.045	0.670	0.089	0.241	0.000
3.00	0.23	0.034	0.653	0.098	0.250	0.000
3.50	0.24	0.003	0.644	0.102	0.254	0.000
4.00	0.245	0.049	0.640	0.104	0.256	0.000

The rate of the reverse reaction was neglected based on two considerations. Firstly, most of the dehydration models published (4,16) have neglected the reverse reaction based on thermodynamic considerations and secondly the heats of formation for dibenzyl ether was not available in the literature. An attempt was made to estimate the heat of formation based on group contribution methods but the values obtained for similar compounds did not match with the reported values.

The isothermal rate expressions for both single site and dual site mechanisms with different controlling steps and with the assumption of an irreversible reaction are given below:

A. Single-site Mechanism:

<u>Rate Controlling Step</u>	<u>Rate Equation</u>
1. Adsorption of A	$kK_A p_A / (1 + K_R p_R + K_S p_S)$
2. Surface Reaction	$kK_A p_A / (1 + K_A p_A + K_R p_R + K_S p_S)$
3. Desorption of R and S	k

B. Dual-Site Mechanism

<u>Rate Controlling Step</u>	<u>Rate Equation</u>
1. Adsorption of A	$kK_A p_A / (1 + K_R p_R + K_S p_S)$
2. Surface Reaction	$kK_A p_A / (1 + K_A p_A + K_R p_R + K_S p_S)^2$
3. Desorption of R and S	k.

Initial discrimination among the rival models was done on the basis of the effect of inlet partial pressure of benzyl alcohol on the initial rate for very low conversions. For low conversions, $P_R \approx P_S \approx 0$ and the rate equations for adsorption of A controlling (Models A1 and B1) reduce to

$$-r_{Ao} = k_A p_{Ao} \quad (3)$$

which predicts a linear dependence of the initial rate with inlet benzyl alcohol partial pressure. The rate data did not follow eqn.(3) and hence models A1 and B1 were discarded. Similarly, for desorption of R and S to control, the rate should be independent of the partial pressure of the reaction products which was again not the case. Therefore, only models with surface reaction controlling were further tested. In addition to models A2 and B2, other models with surface reaction controlling were also checked. The various models which were used for discrimination are given in Table 3.

From the reaction chemistry, with pure benzyl alcohol as feed, P_R will always be equal to P_S and it is not possible to calculate K_R and K_S separately and models 1 to 6 can be simplified by replacing $K_R p_R + K_S p_S$ in the denominator by $K_{RS} p_R$ where K_{RS} is the sum of K_R and K_S . Various investigators have used such simplified models to explain their results. For this study, the values of the kinetic and adsorption equilibrium constants were calculated separately for pure feed and feed containing water.

TABLE 3Final Models for Discrimination

<u>Model</u>	<u>Rate expression</u>	<u>Mechanism</u>
Model 1:	$-r_A = \frac{k K_A p_A}{(1 + K_A p_A + K_R p_R + K_S p_S)}$	(Single Site)
Model 2:	$-r_A = \frac{k K_A p_A}{(1 + K_A p_A + K_R p_R + K_S p_S)^2}$	(Dual Site)
Model 3:	$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_R p_R + K_S p_S)}$	(Single Site)
Model 4:	$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_R p_R + K_S p_S)^2}$	(Dual Site)
Model 5:	$-r_A = \frac{k K_A p_A^2}{(1 + K_A p_A^2 + K_R p_R + K_S p_S)}$	(Single Site)
Model 6:	$-r_A = \frac{k K_A p_A^2}{(1 + K_A p_A^2 + K_R p_R + K_S p_S)^2}$	(Dual Site)

Actual estimation of parameters was done by nonlinear regression analysis of the data using an algorithm for finding minimum of sum of squares of M nonlinear functions in N variables using the Gauss-Newton technique. With pure alcohol (Case as feed, Models 1, 2 and 4 gave results which could be physically interpreted i.e. the kinetic constant increased whereas the adsorption equilibrium constants decreased with temperature. These three models (with K_R and K_S separated out) were then tested for the runs with feed containing water (Case 2) and only Model 4 could represent the data adequately. For Models 1 and 2 the adsorption equilibrium constants came out to be negative at some temperatures. Thus, Model 4 could represent the data for both cases. However, the constants obtained for the two cases were quite different. Strictly speaking, the two models should give the same values with K_{RS} in Case 1 equal to $(K_R + K_S)$ of Case 2.

The values of constants at the different temperatures for the two cases are shown in Tables 4 and 5 respectively. A possible reason for this difference could be the importance of the reverse reaction for the second case.

TABLE 4

Kinetic and Adsorption Equilibrium Constants for Model 4
for Pure Benzyl Alcohol Feed

Temp., °K	k	K_A	K_{RS}
563	8.065	34.343	194.347
583	12.047	21.287	154.505
603	15.370	20.486	114.080
623	17.990	15.579	90.834

TABLE 5

Kinetic and Adsorption Equilibrium Constants for Model 4
for Feed Benzyl Alcohol Containing Water

Temp., °K	k	K _A	K _R	K _S
563	10.01	50.02	250.07	150.23
583	29.73	30.07	230.79	150.11
603	80.53	5.59	242.22	63.49

The activation energies and the heats of adsorption were obtained from the slopes of the Arrhenius Plots and these plots for both cases are shown in Figures 11 and 12 respectively. The preexponential factors and the activation energies for the two cases are shown in Table 6.

The activation energy for k for case 1 is somewhat low but activation energies of the same order of magnitude have been calculated for dehydrogenation of benzylalcohol (16).

The model predicted the experimental rates adequately and Figure 13 shows the comparison between the predicted and experimental rates at 563°K for pure benzyl alcohol feed.

Parameter Estimation for Pyridine Loaded Catalyst:

The rate equation obtained for the fresh catalyst was tested for the experimental data (with $p_R = p_S$) and fitted satisfactorily. The rate equation for the case of mixed feed could not be tested because of computer problems. Actual convergence could be achieved for three temperatures only and the rate constants calculated are shown in Table 7.

The activation energies for the various constants were found from an Arrhenius plot of this data and these can be expressed as

$$k = 36.49 \exp(-3.38/RT_g) \quad (4)$$

$$K_A = 118.52 \exp(5.96/RT_g) \quad (5)$$

$$K_{RS} = 341.78 \exp(4.87/RT_g) \quad (6)$$

where $R_g = 1.987 \times 10^{-3}$ Kcal.

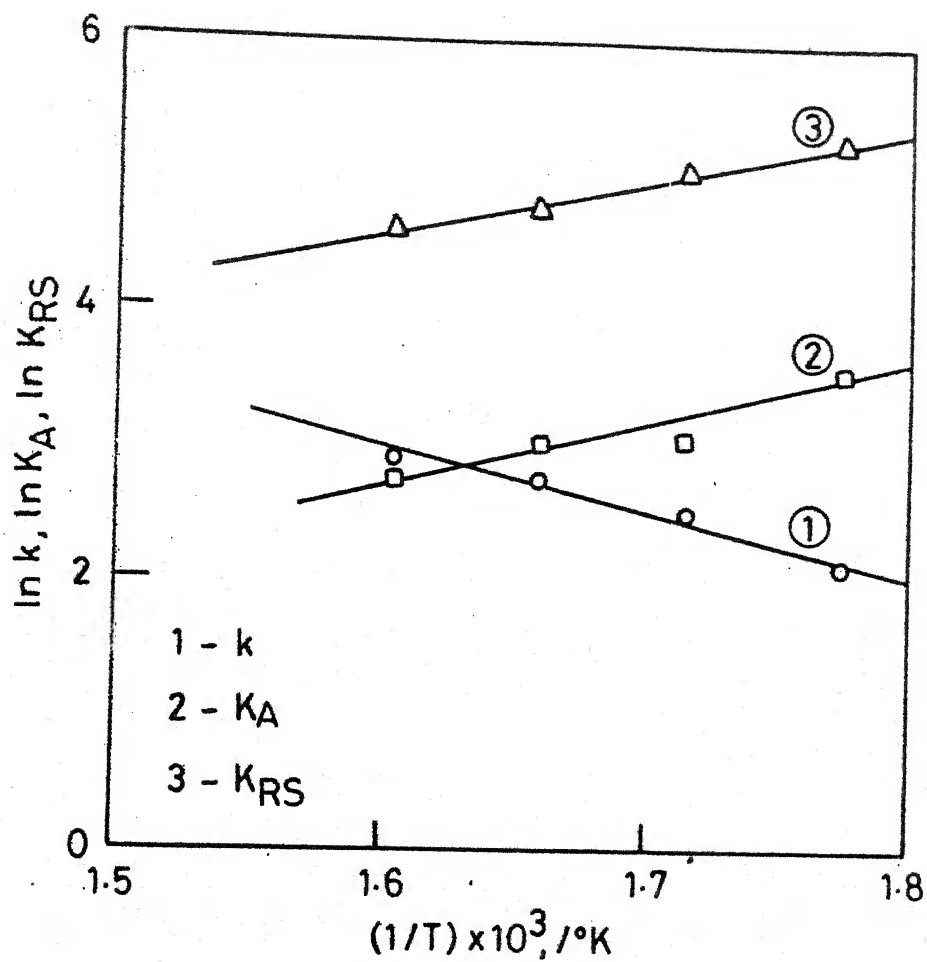


Fig. 11 - Arrhenius plots for the kinetics with pure benzyl alcohol feed on fresh catalyst.

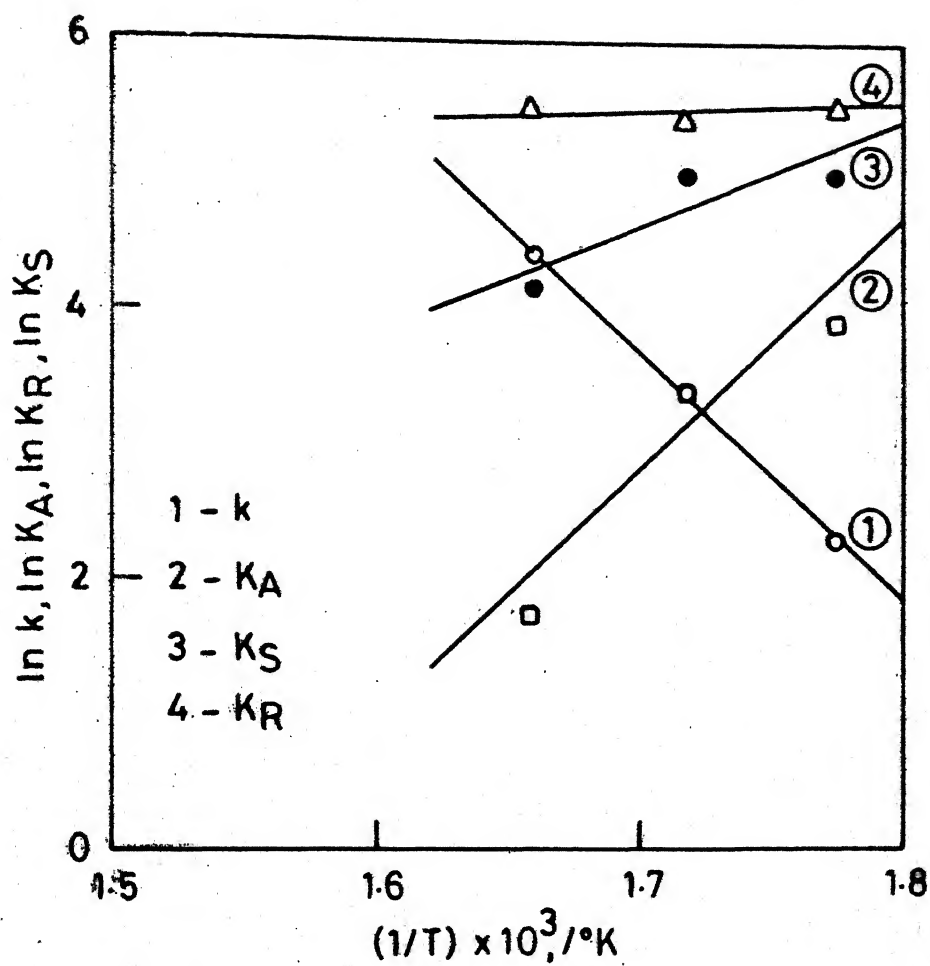


Fig. 12 - Arrhenius plots for the kinetics with feed benzyl alcohol containing water on fresh catalyst.

TABLE 6Preexponential Factor and Activation Energies for the Kinetic and Adsorption Equilibrium Constants

Case 1 : Pure Feed

Rate/Adsorption Equilibrium Constant	Preexponential Factor	Activation, Energy, Kcal
k	12.08	9.935
K_A	24.00	9.339
K_{RS}	142.14	7.948

Case 2 : Mixed Feed

Rate/Adsorption Equilibrium Constant	Preexponential Factor	Activation Energy, Kcal
k	43.33	36.263
K_A	17.33	37.753
K_R	242.67	1.987
K_S	102.84	15.400

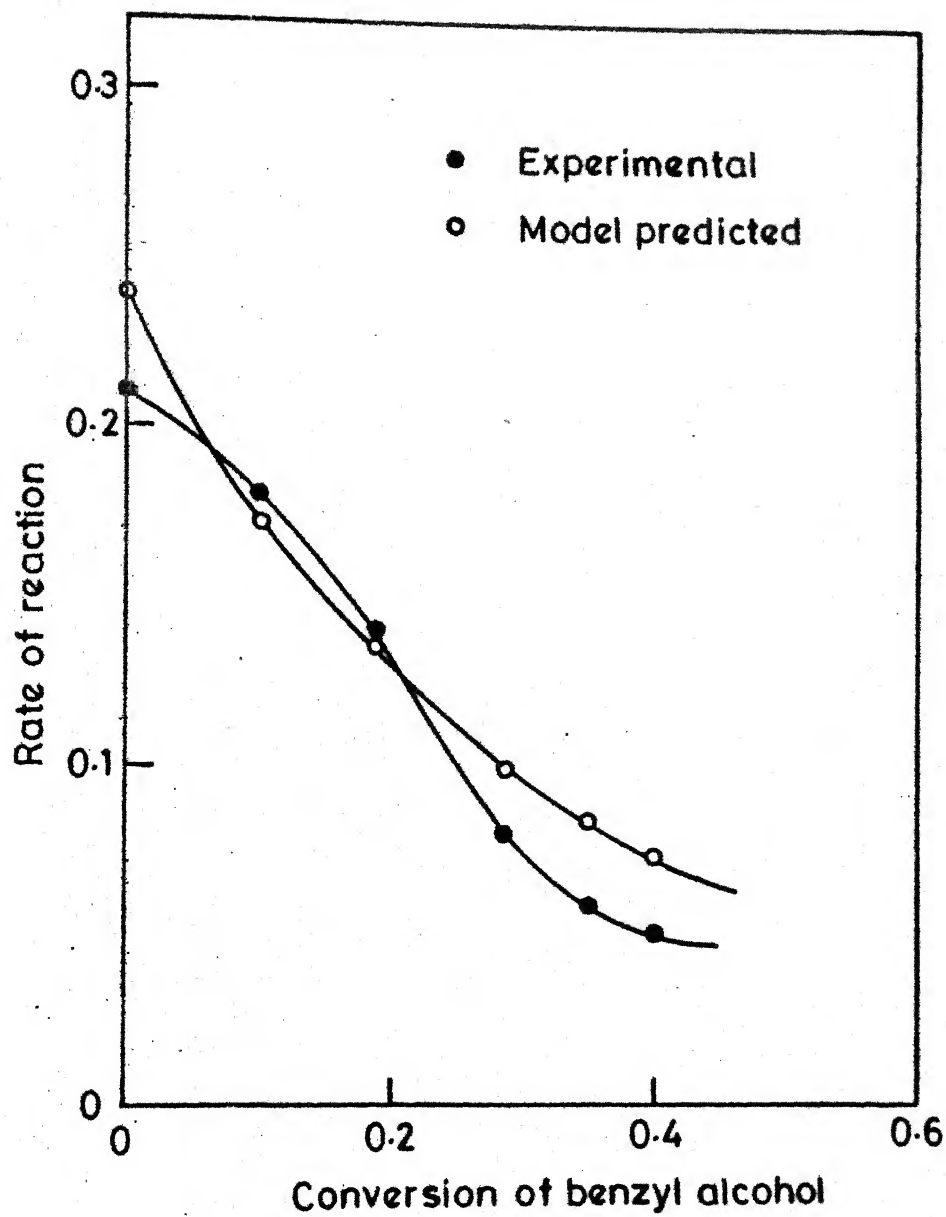


Fig. 13 - Comparison of experimental rates with model predicted rates.

TABLE 7

Kinetic and Adsorption Equilibrium Constants for Pure
Benzyl Alcohol Feed for Pyridine Loaded Catalyst

Temp. °K	k	K_A	K_{RS}
563	29.88	145.12	391.11
583	36.84	123.29	359.83
623	37.45	88.31	257.04

The Arrhenius plots are shown in Figure 14. Compared to the fresh catalyst, all the three constants (k , K_A and K_{RS}) change which indicates that most probably pyridine is affecting the nature of the active sites. However, further work is needed before this can be ascertained.

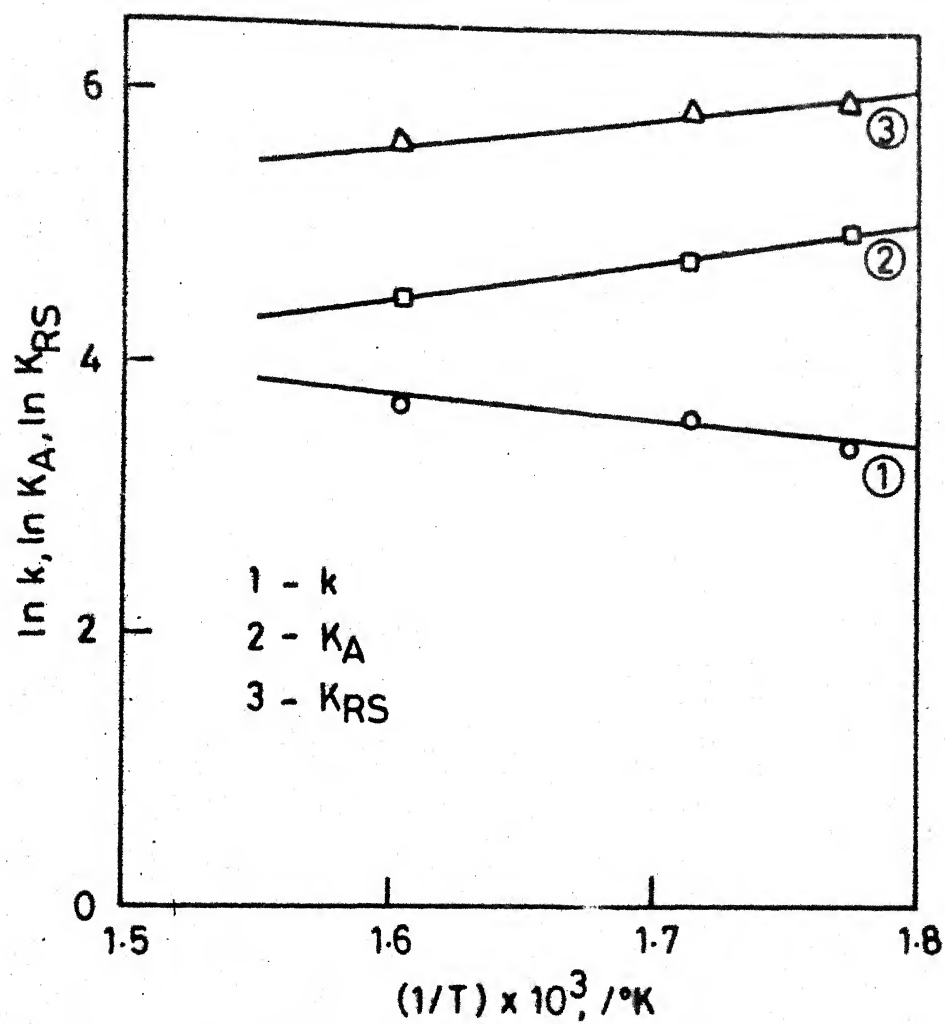


Fig.14 - Arrhenius plots for the kinetics with pure benzyl alcohol feed on pyridine loaded catalyst.

CHAPTER VI

CONCLUSION AND RECOMMENDATION

A study of the kinetics of the gas phase dehydration of benzyl alcohol has been made on γ -alumina catalyst and the effect of pyridine loading on the γ - Al_2O_3 catalyst has also been investigated. A small amount of pyridine on the catalyst increased the conversion of benzyl alcohol significantly although the pyridine was expected to poison the catalyst.

The studies were made in the temperature range 563-623°K for both fresh and pyridine loaded γ - Al_2O_3 with both pure benzyl alcohol feed and feed benzyl alcohol containing water. The expressions

$$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_{RS} p_R)^2} \quad (1)$$

and

$$-r_A = \frac{k K_A p_A^{1/2}}{(1 + K_A p_A^{1/2} + K_R p_R + K_{SP_S})^2} \quad (2)$$

could adequately represent the experimental results for the cases $p_R = p_S$ and $p_R \neq p_S$ respectively.

The rate constants were affected quite significantly for the pyridine loaded catalyst. It appears that pyridine is adsorbing on the Lewis acid sites of alumina which do not catalyze the reaction. Detailed study with different pyridine

loading on catalyst as well as with pyridine in the feed using fresh catalyst need be done as well as some spectroscopic analysis are required to unveil this unnatural phenomenon.

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APPENDIX I

TABLE 8

Rate and Partial Pressure Data for Pure Benzyl Alcohol
Feed for Pyridine Loaded Catalyst

Temperature = 623°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.485	0.735	0.000	0.000	0.265
0.25	0.11	0.388	0.655	0.040	0.040	0.265
0.50	0.20	0.326	0.590	0.072	0.072	0.265
0.75	0.27	0.285	0.534	0.100	0.100	0.265
1.00	0.34	0.257	0.484	0.125	0.125	0.265
1.50	0.46	0.219	0.397	0.169	0.169	0.265
2.00	0.56	0.185	0.323	0.206	0.206	0.265
2.50	0.64	0.153	0.261	0.237	0.237	0.265
3.00	0.71	0.128	0.209	0.262	0.262	0.265
3.50	0.77	0.115	0.165	0.285	0.285	0.265
4.00	0.83	0.101	0.125	0.305	0.305	0.265
4.50	0.87	0.047	0.095	0.319	0.319	0.265

Contd....

Table 8 (Continued):

Temperature = 603°K

W/F_{A0}	X_A	$-r_A$	P_A	P_R	P_S	P_N
0.00	0.00	0.423	0.735	0.000	0.000	0.265
0.25	0.09	0.317	0.668	0.033	0.033	0.265
0.50	0.16	0.269	0.615	0.060	0.060	0.265
0.75	0.23	0.249	0.168	0.084	0.084	0.265
1.00	0.29	0.237	0.523	0.106	0.106	0.265
1.50	0.40	0.212	0.440	0.147	0.147	0.265
2.00	0.50	0.179	0.368	0.183	0.183	0.265
2.50	0.58	0.153	0.308	0.213	0.213	0.265
3.00	0.65	0.140	0.254	0.240	0.240	0.265
3.50	0.72	0.123	0.205	0.265	0.265	0.265
4.00	0.77	0.094	0.165	0.285	0.285	0.265
4.50	0.82	0.103	0.132	0.301	0.301	0.265

Contd....

Table 8 (Continued):

Temperature = 583°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.340	0.735	0.000	0.000	0.265
0.25	0.08	0.297	0.674	0.030	0.030	0.265
0.50	0.15	0.260	0.623	0.056	0.056	0.265
0.75	0.21	0.229	0.579	0.078	0.078	0.265
1.00	0.27	0.204	0.539	0.098	0.098	0.265
1.50	0.36	0.167	0.471	0.132	0.132	0.265
2.00	0.44	0.145	0.414	0.160	0.160	0.265
2.50	0.50	0.134	0.363	0.186	0.186	0.265
3.00	0.57	0.127	0.316	0.210	0.210	0.265
3.50	0.63	0.121	0.270	0.232	0.232	0.265
4.00	0.69	0.110	0.227	0.254	0.254	0.265
4.50	0.74	0.091	0.190	0.272	0.272	0.265

Contd....

Table 8 (Continued):

Temperature = 563°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.268	0.735	0.000	0.000	0.265
0.25	0.06	0.208	0.691	0.022	0.022	0.265
0.50	0.11	0.178	0.656	0.039	0.039	0.265
0.75	0.15	0.164	0.625	0.055	0.055	0.265
1.00	0.19	0.157	0.596	0.069	0.069	0.265
1.50	0.26	0.147	0.540	0.098	0.098	0.265
2.00	0.33	0.133	0.488	0.123	0.123	0.265
2.50	0.40	0.119	0.442	0.146	0.146	0.265
3.00	0.45	0.110	0.400	0.167	0.167	0.265
3.50	0.51	0.104	0.360	0.187	0.187	0.265
4.00	0.56	0.096	0.323	0.206	0.206	0.265
4.50	0.60	0.086	0.290	0.222	0.222	0.265

TABLE 9

Rate and Partial Pressure Data for Feed Benzyl Alcohol
Containing Water for Pyridine Loaded Catalyst

Temperature = 623°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.486	0.735	0.000	0.152	0.113
0.25	0.11	0.389	0.654	0.040	0.192	0.113
0.50	0.19	0.306	0.591	0.072	0.224	0.113
0.75	0.26	0.245	0.541	0.097	0.249	0.113
1.00	0.32	0.207	0.499	0.119	0.270	0.113
1.50	0.41	0.178	0.430	0.152	0.304	0.113
2.00	0.50	0.167	0.367	0.184	0.336	0.113
2.50	0.58	0.141	0.309	0.213	0.365	0.113
3.00	0.64	0.107	0.264	0.235	0.387	0.113
3.50	0.69	0.094	0.228	0.253	0.405	0.113
4.00	0.74	0.108	0.191	0.272	0.424	0.113
4.50	0.78	0.038	0.158	0.288	0.440	0.113

Contd...

Table 9 (Continued):

Temperature = 603°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.414	0.735	0.000	0.152	0.113
0.25	0.08	0.285	0.672	0.031	0.183	0.113
0.50	0.15	0.219	0.626	0.054	0.206	0.113
0.75	0.20	0.188	0.589	0.073	0.225	0.113
1.00	0.24	0.177	0.556	0.089	0.241	0.113
1.50	0.33	0.168	0.493	0.121	0.273	0.113
2.00	0.41	0.156	0.433	0.151	0.303	0.113
2.50	0.48	0.138	0.379	0.178	0.330	0.113
3.00	0.55	0.125	0.331	0.202	0.354	0.113
3.50	0.61	0.116	0.286	0.224	0.376	0.113
4.00	0.66	0.102	0.246	0.244	0.396	0.113
4.50	0.71	0.077	0.213	0.261	0.413	0.113

Contd....

Table 9 (Continued):

Temperature = 583°K

W/F_{A0}	X_A	$-r_A$	p_A	p_R	p_S	p_N
0.00	0.00	0.321	0.735	0.000	0.152	0.113
0.25	0.07	0.235	0.685	0.025	0.177	0.113
0.50	0.12	0.202	0.645	0.045	0.197	0.113
0.75	0.17	0.190	0.609	0.063	0.215	0.113
1.00	0.22	0.181	0.575	0.080	0.232	0.113
1.50	0.30	0.153	0.513	0.111	0.263	0.113
2.00	0.37	0.123	0.463	0.136	0.288	0.113
2.50	0.43	0.113	0.420	0.157	0.309	0.113
3.00	0.49	0.118	0.377	0.179	0.331	0.113
3.50	0.54	0.108	0.325	0.202	0.352	0.113
4.00	0.59	0.076	0.301	0.217	0.369	0.113
4.50	0.63	0.140	0.268	0.233	0.385	0.113

Contd....

Table 9 (Continued):

Temperature = 563°K

W/F_{A0}	X_A	$-r_A$	P_A	P_R	P_S	P_N
0.00	0.00	0.218	0.735	0.000	0.152	0.113
0.25	0.05	0.161	0.701	0.017	0.169	0.113
0.50	0.08	0.138	0.674	0.030	0.182	0.113
0.75	0.12	0.132	0.649	0.043	0.195	0.113
1.00	0.15	0.132	0.625	0.055	0.207	0.113
1.50	0.21	0.127	0.577	0.079	0.231	0.113
2.00	0.27	0.114	0.532	0.101	0.253	0.113
2.50	0.33	0.104	0.493	0.121	0.272	0.113
3.00	0.38	0.100	0.455	0.140	0.292	0.113
3.50	0.43	0.096	0.419	0.158	0.310	0.113
4.00	0.47	0.084	0.386	0.174	0.336	0.113
4.50	0.51	0.082	0.356	0.189	0.341	0.113

APPENDIX II

CALIBRATION CURVES FOR CHROMATOGRAPHIC ANALYSIS

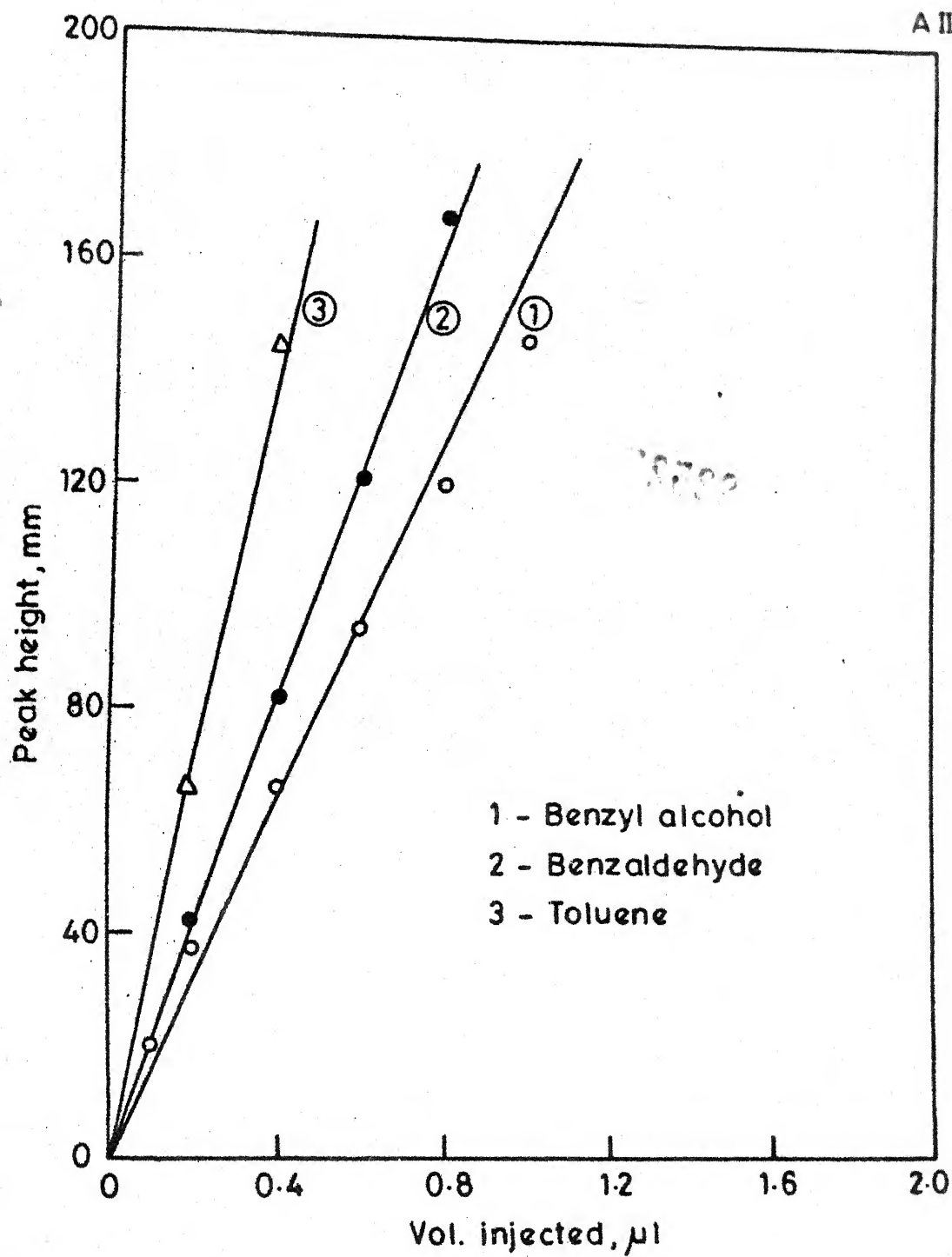


Fig. 15 - Calibration curve for chromatographic analysis.

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